The reduction of perchlorate by hydrogenation catalysts

Rovshan Mahmudov [a], Yuying Shu [b,1], Sergei Rykov [b],
Jingguang Chen [b], Chin Pao Huang [a,*]

[a] *Department of Civil and Environmental Engineering, University of Delaware, 301 DuPont Hall, Newark, DE 19702, USA*
[b] *Department of Chemical Engineering, University of Delaware, 332 CLB 50 Academy Street, Colburn Laboratory,
University of Delaware Newark, DE 19716, USA*

Abstract

Perchlorate competes with thyroid uptake of iodide, an essential nutrient for the production of thyroid hormones. Despite the extensive attempts to reduce perchlorate in aqueous solution, the process is slow and requires high temperatures even in the presence of catalysts. Therefore, perchlorate reduction under hydrogen atmosphere was employed. Monometallic and bimetallic Pt based catalysts (e.g., Pt/C, Ni-Pt/C, Co-Pt/C, and W-Pt/C) supported on activated carbon were prepared by successive incipient wet impregnation method and used for gas-phase reduction of perchlorate pre-adsorbed onto the activated carbon. The catalysts were characterized for hydrogen chemisorption and XPS. Hydrogen uptake was in the order: Co-Pt/C > W-Pt/C ≈ Pt/C > Ni-Pt/C. The least H_2 uptake by Ni-Pt/C was likely due to lower dispersion on activated carbon surface with 11.5% vs. 36% for Pt/C. There was a good correlation between hydrogen uptake by impregnated activated carbon (IAC) and perchlorate reduction. The Co-Pt/C exhibited the highest hydrogen uptake and the best perchlorate reduction while Ni-Pt/C was the least reducing system. When Co-Pt/C was used almost 90% of perchlorate was reduced at 25 °C and initial surface concentration of perchlorate of 11.47 mg g^{-1} in 24 h. The reaction rate increased 10-folds when the reaction temperature was raised to 75 °C. In 24 h reaction time, increase of temperature from 25 to 75 °C resulted in additional 10% (Co-Pt/C) and 30% (Ni-Pt/C) increase in perchlorate reduction for Co-Pt/AC and Ni-Pt/AC, respectively, which brought the reduction efficiency close to 100%. The only reaction product that evolved was Cl$^-$, indicating that the cleavage of the first oxygen atom of perchlorate was the rate-limiting step. The lowest activation energy for the reduction of perchlorate was 39.5 kJ mol^{-1} for Co-Pt/C. Results also showed that the activation of gaseous hydrogen molecules on metal catalysts was the major reducing step, although deposited metals also participated in the perchlorate reduction directly. Results of XPS analysis revealed that during adsorption/reduction some portion of the second metal in the bimetallic catalysts was lost due to dissolution while Pt was very stable.
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1. Introduction

Although the toxicity of perchlorate and its occurrence in public drinking water systems has been extensively investigated before the 1990s, it is revised only recently after the development of more sensitive analytical techniques that allowed detecting perchlorate at the ppb levels. Perchlorate is suspected of disrupting the thyroids uptake of iodide, an essential nutrient for the synthesis of thyroid hormones, and subsequently causing the malfunction of metabolic processes

[1,2]. Perchlorate was included in the EPA's candidate contaminant list (CCL) with reference dose of 0.0007 mg/kg-d of body weight, which is equivalent to 24 ppb in drinking water [3]. Most widely used applications of perchlorate are oxidant in solid fuel rocket propellants, explosives, pyrotechnics, and to a lesser extend in the manufacture of commercial products ranging from electronics to pharmaceuticals. Therefore, perchlorate contamination of source water is mostly linked to military and airspace activities.

Reduction of perchlorate has represented a challenge for the chemical and environmental professionals for decades. Chemical and electrochemical reduction of perchlorate are among the most appealing processes due to the ease in operation and wide public acceptance. In these processes,

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transition metals were frequently used either as direct electron donors or as catalysts that facilitate the electron transfer. It is a controversy in chemical reaction kinetics that strong metallic reducing agents such as Cr^{2+}, Eu^{2+}, Sn^{2+}, and Fe^{2+} do not react with perchlorate at any measurable rates under environmentally relevant conditions, whereas much weaker reductants such as Ti^{3+} and Ru^{2+} show better capability in perchlorate reduction [4,5]. At room temperature perchlorate ion was found to be reduced to chloride at measurable rates by titanium(III) [6], vanadium(II) and vanadium(III) [7], ruthenium(II) [8], and Mo^{3+} and aqua dimmer $[Mo(III)]_2$ [5]. It was found that although Cr^{2+} ($Cr^{2+} = Cr^{3+} + e$; $E^{\circ}_{(NHE)} = -0.41$ V) and Eu^{2+} ($Eu^{2+} = Eu^{3+} + e$; $E^{\circ}_{(NHE)} = -0.43$ V) are strong reducing agents, their reaction with perchlorate is extremely slow with rate constant $<10^{-8}$ M^{-1} s^{-1} [9] and all reactions required low pH of 2 and high concentrations (>0.2 M) of reactants. Perchlorate reduction by iron(II) at elevated temperatures has been reported [10]. Complete perchlorate reduction occurred in approximately 3 and 1 h at 170 and 195 °C, respectively. Elemental iron also showed capability of reducing perchlorate [11,12]. Moore et al. studied perchlorate reduction by elemental iron and concluded that perchlorate was first adsorbed onto iron surface and then was reduced [12]. Perchlorate reduction up to 66% occurred after 336 h. It was speculated that neither zero-valent iron nor iron oxides reduced perchlorate but the surface complexes of Fe^{2+} on the iron particle most probably was responsible for perchlorate reduction.

Catalytic hydrogenation of perchlorate has also been reported. Study of electrochemical reduction of perchlorate on Pt and WC electrodes suggested that perchlorate was partially reduced by catalytic hydrogenation [13,14]. Overall reaction rates, however, were too slow to be of significance in treatment applications. Butula and Butula [15] reported perchlorate reduction by acetic acid in the presence of Pd/$BaSO_4$ and Rh/C catalysts at 60 °C. Under mild conditions oxoruthenium (V) was shown to catalyze perchlorate reduction by organosulfides [16]. Perchlorate was completely reduced in 4–7 h. Hydrogen gas is a more benign reducing agent than transition metals and organic compounds as electron donors in variety of reduction processes. Recently, Hurley and Sharpley [17] developed a Pd based bimetallic catalyst with Rhenium (VII) precursor that efficiently catalyzed the reduction of perchlorate by hydrogen gas. However, the best reduction efficiency was achieved at pH <3; the method was most suitable for the treatment of acidic wastes containing perchlorate.

Hydrogenation catalysts such as Pd and Pt and their bimetallic forms have been shown to be effective for the reduction of nitrate and nitrite in drinking water [18,19]. Best results for nitrate and nitrite reduction was observed with Pd and Pt catalysts and Cu as a promoter. The various combinations of catalysts, promoters, and preparation methods also affected the selective formation of N_2 over NH_4^+ [18]. Recently, it has been shown that Pt bimetallic catalysts can increase the hydrogenation activity compared to monometallic Pt catalyst. For example, Co/Pt and Ni/Pt bimetallic catalysts increased the hydrogenation activity when compared to

monometallic Pt catalyst. Due to unique electron properties Pt based bimetallic catalysts have been found to be very efficient in the hydrogenation of organic compounds [20–22]. The increase in activity of novel bimetallic catalysts was believed to be due to modification of the Pt d-band by the subsurface metal. Various support materials have been used for the preparation of these catalysts. Most widely used are the inorganic substrates such as Al_2O_3 [23,24] and TiO_2 [25]. Activated carbon also has been used as a catalyst support due to advantages of large specific surface area. Furthermore, it has been reported that activated carbon impregnated with hydrogenation catalysts showed superior affinity for hydrogen adsorption compared to virgin activated carbon (VAC) [26]. Increase in hydrogen adsorption of activated carbon impregnated with catalyst was shown to be due hydrogen chemisorption on the hydrogenation metals.

Despite the good efficiency of nitrate reduction, the reduction of perchlorate by hydrogen gas in the presence of catalysts was found to be very slow [27,28]. The major reason is that perchlorate does not accept electrons through outer sphere complex formation and it hardly forms inner sphere complexes in dilute aqueous solutions. Inner sphere complex formation and distortion of perfect tetrahedral symmetry of perchlorate is necessary in order for perchlorate to react [6]. In the present study, first we hypothesized that perchlorate adsorption onto activated carbon will result in distortion of the tetrahedral symmetry of perchlorate, which will bring about perchlorate reduction. Second, use of catalyst can facilitate electron transfer from hydrogen to the perchlorate. Third, under the context of the second hypothesis, bimetallic catalysts will be more efficient than monometallic catalysts in the perchlorate reduction.

2. Experimental

2.1. Preparation of catalysts

A series of Pt based mono- and bimetallic (Pt with Ni, Co, and W) catalysts supported on activated carbon were prepared by the successive incipient impregnation method at 5% dry weight of Pt loading and a Pt to second metal atomic ratio of 1:1. The catalysts are designated as follows: monometallic Pt catalyst as Pt/C, and bimetallic catalysts Ni and Pt as Ni-Pt/C, Co and Pt as Co-Pt/C, and W and Pt as W-Pt/C.

The support was activated carbon Filtrasorb F400 from Calgon Carbon Co. Filtrasorb F400 is a granular bituminous coal based activated carbon with average grain size of 12×40 meshes and denoted as virgin activated carbon. To remove surface impurities and reduce ash content the VAC was first washed once with 1 mM HNO_3 and three times with 1 mM NaOH. Then the washed VAC was rinsed with sufficient amount of distilled deionized water (DDW) (17.8 MΩ cm) until the rinse water reaching a constant conductivity close to that of the distilled water. The VAC was then dried under air at 37 °C overnight, evacuated under vacuum for 4 h at 100 °C and stored in desiccator.

Chemicals used in the synthesis of catalysts were $Pt(NH_3)_4(NO_3)_2$ (Alfa Aesar 99.999%), $Co(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, 99.999%), $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, 99.9985%), and $(NH_4)_2WO_4$ (Alfa Aesar, 99.99%). The incipient wetness point for activated carbon was determined to be 0.8 cm^{-3} g^{-1}. In the case of Pt/C, a quantity of 0.9924 g of $Pt(NH_3)_4(NO_3)_2$ was dissolved in the calculated volume (10 mL) of DDW to form a transparent solution, then the Pt solution was added to 10 g of VAC support drop wise in order to keep the homogeneity of the resulting materials. In the case of Co-Pt/C, a quantity of 0.9924 g of $Pt(NH_3)_4(NO_3)_2$ and 0.7459 g of $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in the same calculated volume (10 mL) of distilled water to form a transparent solution, then sequentially added to 10 g of support drop by drop. The impregnated activated carbon (IAC) was kept at room temperature overnight, dried at 383 K for 5 h, and annealed at 563 K for 2 h in air. Supported catalysts were then reduced under H_2 flow at 573 K for 24 h, cooled to room temperature, and stored in desiccator under N_2 atmosphere.

2.2. Perchlorate adsorption and reduction

The IAC (0.5 g) was first saturated with 100 mL of aqueous ammonium perchlorate solution at initial concentrations of 10, 30, 50, or 100 ppm for 24 h. Then the supernatant was obtained by vacuum filtration on 0.45-μm membrane filter (Millipore) and analyzed for residual perchlorate. The amount of perchlorate adsorbed was determined by the difference between initial and final perchlorate concentrations. The separated IAC was placed in the reaction cell and purged with N_2 at room temperature for 2 h to remove excess water. The reaction cell was a 16-mm glass joint with glass frit. After purging the cell was placed in the oven and 10% H_2 + 90% N_2 gas was applied at flow rate of 15 mL/min and the temperature was adjusted to desired value within ± 1 °C. The exhaust was passed through the gas scrubber to collect the reaction products in the gas flow. The treatment time is referred to the moment at which the hydrogen gas was applied. After certain reaction time the oven was cooled to room temperature, the sample removed, and regenerated in NaOH solution at pH of 11 for 24 h. After the regeneration the supernatant was withdrawn and analyzed to determine the amount of perchlorate and the reaction products. The amount of perchlorate that was reduced was determined by the difference in the concentration initially present on the surface (amount adsorbed) and the amount extracted during the regeneration process.

2.3. Analysis

The H_2 chemisorption experiments of supported catalysts were carried out using an Altamira Instruments AMI-200ip. The sample of 0.1 g of IAC was loaded in a quartz reactor and reduced in dilute hydrogen (50% H_2/He) at 723 K for 1 h. After the reduction of the catalysts the flow was switched to helium at 723 K and was kept at this temperature for 10 min. Then the temperature was lowered to 298 K under the He flow. After cooling in He for 30 min, pulses of H_2 in a He carrier gas at 20 cm^3 min^{-1} were injected at 298 K through a sample loop and the signal was monitored with a thermal conductivity detector (TCD). The H_2 uptake and metal dispersion were calculated by measuring the decrease in the peak areas as a result of adsorption and compared with the peak area of a calibrated volume (58 μmol). The catalyst dispersion was calculated assuming a stoichiometry of one hydrogen atom per surface metal atom. Surface area and pore size distribution of virgin and impregnated activated carbons were analyzed using high-speed gas analyzer Nova 2000 from Quantachrome by the BET method. Before surface area measurements the activated carbons were degassed under vacuum at 473 K overnight.

The XPS was collected on PerkinElmer ESCA 5500 with monochromatic Al Kα X-ray source. Pass energy and time step were 49.95 eV and 1000 ms and 23.5 eV and 1000 ms for survey scan and high resolution scans, respectively. The IAC were grinded and placed on tungsten plate for XPS analysis. Before the XPS analysis the IAC were evacuated in the introduction chamber for 24 h to evacuate volatile compounds present on the surface. The XPS spectra were collected for supported catalysts before and after reduction experiments.

Analysis of perchlorate and other reaction products was carried out by IC Dionex 500. The IC was equipped with AS11 chromatographic column, AG 11 guard column, and ASRS Ultra anion suppressor operated in external chemical suppression mode.

3. Results and discussion

3.1. Hydrogen uptake by mono- and bimetallic catalysts

The hydrogenation of perchlorate requires the dissociative adsorption of hydrogen on the catalysts. Tagaki et al. has discussed the mechanism of H_2 adsorption on activated carbon fibers impregnated with Pt and Pd catalysts [26,29]. The higher hydrogen uptake on impregnated activated carbon surface compared to that of virgin activated carbon was attributed to enhanced hydrogen chemisorption on the metallic catalyst present at IAC. Results also showed that hydrogen adsorption was completely reversible. The development of novel bimetallic catalysts resulted in a whole array of new chemical properties distinctly different from parent metals. For example, when the Pt surface was modified with one monolayer of Co and Ni, hydrogen was desorbed at lower temperatures which indicated the formation of weaker bonds as compared to those of single Pt, Co, or Ni catalysts [30–32].

The hydrogen adsorption capacity of catalysts is closely related to the dispersion of metal in its support. The dispersion of catalyst is defined as the ratio of the number of atoms on the surface (n_s) to the number of atoms in the bulk (n_b). The number of surface atoms was determined from hydrogen chemisorption data assuming that one hydrogen atom was sorbed per one catalyst atom. Table 1 shows the results of hydrogen chemisorption on IAC and dispersion of catalyst as determined by assuming dissociative adsorption of hydrogen. Results indicated that AC impregnated with Co-Pt bimetallic catalysts had the highest hydrogen adsorption capacity and, respectively,

Table 1
Hydrogen uptake and Pt dispersion of mono- and bimetallic catalysts supported on AC

Sample	A_{sp} (m^2 g^{-1})	V_t(<1000 Å) (mL g^{-1})	V_{mi} (<20 Å) (mL g^{-1})	H$_2$ uptake (μmol g^{-1})	Dispersion[a] (%)
VAC	1250	0.57	0.26	–	–
Pt/C	953	0.56	0.15	47.3	36.9
Ni-Pt/C	1047	0.55	0.14	29.5	11.5
Co-Pt/C	1005	0.57	0.07	73.2	28.6
W-Pt/C	972	0.53	0.16	47.7	18.6

[a] From H$_2$ chemisorption measurements; A_{sp}: the specific surface area; V_t: total pore volume; V_{mi}: the micropore volume.

better dispersion on the carbon surface. Pt/C and W-Pt/C exhibited similar hydrogen uptake, while Ni in the alloy resulted in the decrease in hydrogen uptake capacity. The dispersion of catalyst as measured by H$_2$ chemisorption was in the range of 11.5 for Ni–Pt/C to 36.9 for Pt/C. The presence of the second metal resulted in somewhat poorer dispersion of catalyst on the surface of activated carbon. The dispersion of the bimetallic catalyst Co-Pt/C was less than Pt/C, however, it exhibited hydrogen uptake capacity two times greater than the latter. The W-Pt/C had two times lower dispersion but almost same hydrogen uptake as Pt/C. The dispersion of catalyst on the substrate surface is temperature dependent. Nanba et al. reported that best dispersion of Pt on ZrO$_2$ was achieved in the temperature range 400–700 °C [33]. The dispersion of catalyst decreased dramatically when the annealing temperature exceeded 700 °C. In our experiments the catalyst was only annealed at 563 K (300 °C), which resulted in relatively well-dispersed catalyst.

The BET specific surface area of IAC was slightly smaller than that of the VAC and the total volume of micropores decreased more dramatically than the macropore volume. The catalyst dispersion data indicates that the catalysts were present on the surface in the form of particles rather than molecules. These catalyst particles can block some small pores of the activated carbon, resulting in the observed decrease in the total surface area and micropore volume.

3.2. Perchlorate adsorption on impregnated activated carbon

At the onset of the reduction experiments, the IAC was loaded with perchlorate. Since perchlorate adsorption onto activated carbon was favorable in acidic media, the adsorption of perchlorate onto IAC was conducted at pH of 4. Fig. 1 shows the adsorption of perchlorate on VAC and IAC used in this study. There was almost two-fold decrease in the adsorption of perchlorate on IAC with respect to that on VAC. There are two possible reasons for the decrease in the adsorption of perchlorate on IAC. First, the surface area and total volume of micropores decreased for IAC compared to VAC (Table 1), which indicated that metallic catalysts blocked the micropores that contributed to the major portion of surface area of the activated carbon. Second, calcination may cause surface oxidation of the activated carbons, which will introduce oxygen-containing groups onto the surface thereby changing the surface charge characteristics of the activated carbon [34]. The virgin activated carbon F400 has the pH$_{zpc}$ (point of zero

charge) of 9.2 [35]. The calcination of activated carbon in air at 300 °C resulted in lowering the pH$_{zpc}$ < ~3. This means that the activated carbon will be negatively charged in the pH range of perchlorate adsorption. Intuitively, electrostatic repulsion impeded perchlorate adsorption onto the negatively charged surface.

Perchlorate adsorption on both impregnated and virgin activated carbons followed the Langmuir type of adsorption as presented by the following equation:

$$\equiv C = \frac{\equiv C_m K_s C_e}{1 + K_s C_e} \tag{1}$$

where $\equiv C$ is the amount of perchlorate adsorbed (mg g^{-1}), $\equiv C_m$ is the monolayer adsorption capacity (mg g^{-1}), K_s is the equilibrium constant (L mg^{-1}), and C_e is the bulk equilibrium concentration of perchlorate in solution (mg L^{-1}).

The Langmuir parameters $\equiv C_m$ and K_s were similar for all metal-activated carbon combinations. The average value of $\equiv C_m$ was 11.47 ± 0.76 mg g^{-1} and the average value K_s was 0.14 ± 0.02 L mg^{-1}.

3.3. Gas-phase reduction of perchlorate

An attempt to reduce perchlorate by hydrogen gas in aqueous phase at the same conditions as reported herein for the gas-phase reduction was not successful. Perchlorate reduction (not given) was approximately 5% at 50 °C in 72 h. The reduction was dramatically improved when impregnated activated carbon after
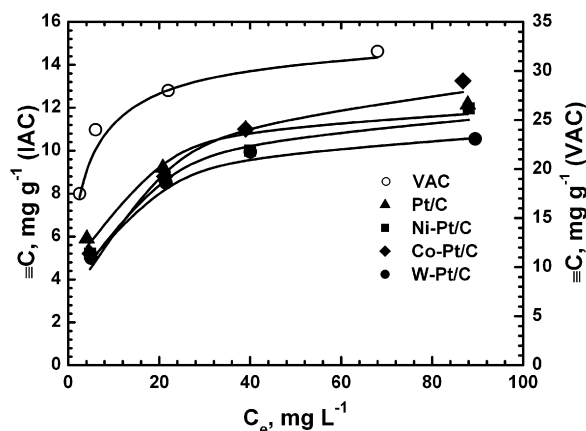

Fig. 1. Adsorption of perchlorate on plain and impregnated activated carbons. Lines represent the Langmuirian fit: $\equiv C_m$ (IAC) = 11.47 ± 0.76 mg L^{-1} and K_s (IAC) = 0.14 ± 0.02 L mg^{-1}; $\equiv C_m$ (VAC) = 32.11 mg g^{-1} and K_s (VAC) = 0.45 L mg^{-1}. Experimental conditions: pH 4, $I = 10^{-2}$ M NaCl, $T = 25$ °C, [VAC] = 1 g L^{-1}, [IAC] = 5 g L^{-1}.
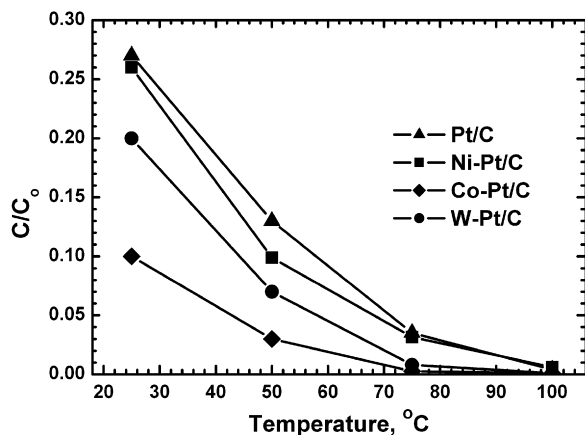
Fig. 2. Effect of temperature on gas-phase reduction of perchlorate on Pt based catalysts supported on activated carbon. Conditions: gas flow rate: 15 mL/min, duration: 24 h, amount of ClO_4^- adsorbed ($\equiv C_o$) = 11.47 ± 0.76 mg ClO_4^- g^{-1}.

being saturated with perchlorate and being separated from water was exposed to hydrogen gas at various temperatures. Fig. 2 shows the effect of temperature on the reduction of perchlorate in 24 h. Substantial amount of perchlorate reduction, from 74 (Ni–Pt/C) to 85% (Co–Pt/C), was observed even at 25 °C in 24 h. It seems that there is a correlation between the hydrogen uptake capacity of IAC and the perchlorate reduction rate. Those catalyst systems that had better hydrogen chemisorption also exhibited better perchlorate reduction. The Co-Pt/C, which had the best hydrogen uptake also showed the best reduction of perchlorate as compared to the Ni-Pt/C catalyst that had the

lowest hydrogen uptake and subsequently the lowest reduction rate of perchlorate. Further increase in temperature enhanced perchlorate reduction to complete degradation.

The temperature played an important role on the reduction kinetics as well. Fig. 3 shows the reduction kinetics of perchlorate at 25, 50 and 75 °C for the four catalysts. Perchlorate reduction at >90% took place in 5 and 2 h at 50 and 75 °C, respectively. The reduction reaction was fast in phase one, which was followed by slow second stage. The Co-Pt catalyst had slightly higher reduction rate than other catalysts. The temperature also affected the degree of perchlorate reduction on the surface of IAC. The final concentration of perchlorate on the surface of IAC after 24 h was 0.42 and 0.21 mg g^{-1} at 50 and 75 °C, respectively, at an initial loading of perchlorate of 11.47 mg g^{-1}.

The reaction kinetics was fitted by the pseudo first order rate equation, since H_2 was supplied continuously during reaction and was assumed to be constant throughout the experiment:

$$\equiv C/C_o = e^{-k'\tau} \tag{2}$$

where $\equiv C/C_o$ is the concentration of perchlorate on the surface at time τ (mg g^{-1}), k' is the pseudo first order rate constant, and τ is time (h).

The pseudo first order rate constant, k', was obtained by least squares analysis. The pseudo first order rate constants were then used to determine the activation energy of perchlorate reduction on IAC using the Arrhenius plot. Fig. 4 gives the linear Arrhenius plot for the four catalysts. The linear relation with $R^2 > 0.96$ was obtained. All catalysts yielded similar slope,
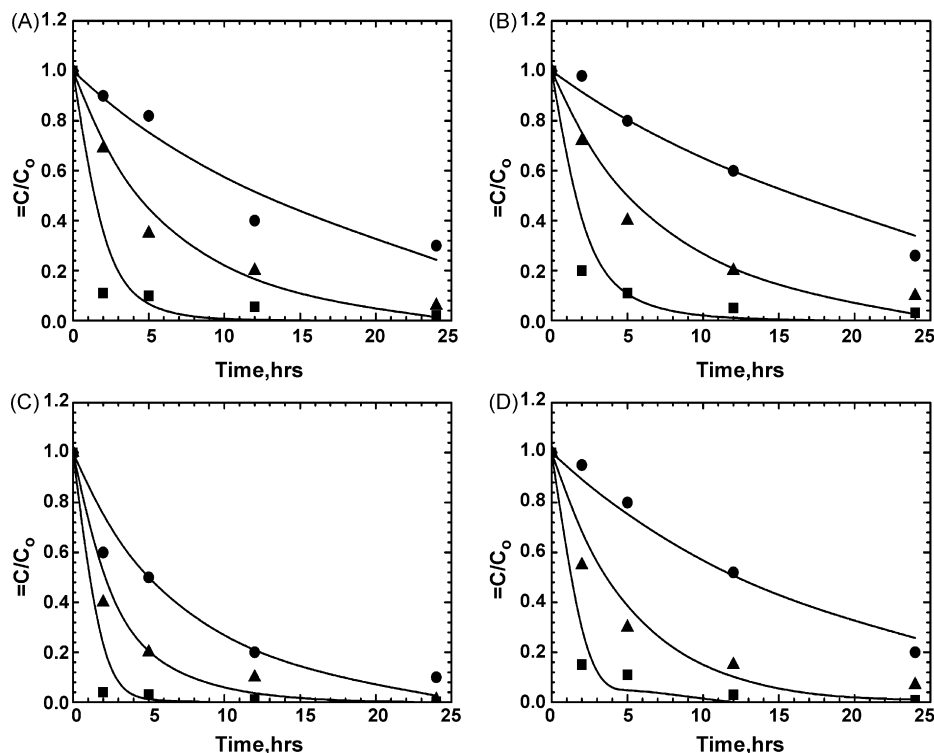

Fig. 3. Effect of temperature on reduction kinetics of perchlorate on Pt based catalysts supported on activated carbon. Symbols: (●) at 25 °C, (▲) at 50 °C, and (■) at 75 °C. (A) Pt/C, (B) Ni-Pt/C, (C) Co-Pt/C, and (D) W-Pt/C. Lines represent fit by pseudo first order rate equation.
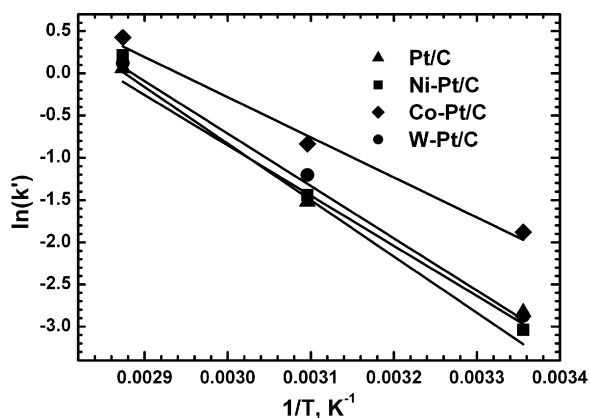
Fig. 4. Arrhenius plot for perchlorate reduction on impregnated activated carbon.

indicative of identical activation energy. Table 2 lists the k' values and the activation energy for Co-Pt/C from this study and those reported by others on different perchlorate reduction systems. The activation energies for Pt/C, Ni-Pt/C, and W-Pt/C were, respectively, 43.3, 39.5, and 41.1 kJ mol^{-1}. Cao et al. reported an activation energy of 79.2 kJ mol^{-1} for the reduction of perchlorate using iron nanoparticles [11]. Gu et al. reported an activated energy of 120 kJ mol^{-1} for perchlorate reduction in FeCl$_3$–HCl solution reported [10].

Good chloride mass balance was observed indicating that chloride was the major end product of the perchlorate reaction as shown in Fig. 5. Among other reaction products, only a small amount (below quantification level of the analysis, e.g., 50 ppb) of ClO$_3^-$ was detected briefly, and then disappeared, as the reaction time was longer than 2 h.

The effect of perchlorate surface loading on the reduction efficiency was studied at 25, 50, and 75 °C and reduction time of 24 h. The reduction efficiency (η) was defined by the following equation:

$$\eta = 1 - (\equiv C/C_o)_\tau \qquad (3)$$

where $(\equiv C/C_o)_\tau$ is relative surface concentration of perchlorate at any time, τ.

Fig. 6 gives the plot of reduction efficiency vs. surface coverage ($\equiv C/C_m$) of IAC with perchlorate at reaction time of 24 h. The reduction efficiency increased almost linearly with increase in surface loading of perchlorate at low temperatures, but the effect of surface loading diminished with increase in temperature. The reduction efficiency increased by three-folds when the initial surface loading ($\equiv C/C_m$) increased from 0.4 to 1.0 ($\equiv C_m = 11.47$ mg g^{-1}) for Ni-Pt/C. There was nearly complete reduction at temperature of 75 °C even when surface loading reached the maximum levels.

3.4. The X-ray photoelectron spectra

Fig. 7 gives the XPS spectra of mono- and bimetallic Pt based catalysts supported on activated carbon. Based on the Pt(4f$_{7/2}$) peak, the binding energy was 71.1, 71.1, 71.1, and 71.4 eV for Pt/C, Co-Pt/C, Ni-Pt/C, and W-Pt/C, respectively. Results indicated that Pt was present in metallic form in both mono- and bimetallic catalysts. Ariclo et al. reported a binding energy of 71.5 eV for Pt catalysts supported on activated carbon [36]. The binding energy for bulk Pt was 70.8 eV; the shift in binding energy for the supported Pt catalysts could be attributed to size and cluster effect [36–38]. Eberhardt et al. showed that the shift could be as large as 3 eV depending on the surface concentration and cluster size of deposited catalysts [37]. There is no apparent shift of Pt 4f$_{7/2}$ between mono- (Pt) and bimetallic Pt/Ni and Pt/Co catalysts, but slightly positive shift (e.g., 0.3 eV) for the W-Pt/C catalyst. The peak corresponding to Pt^o appeared to be stronger for the bimetallic than that of the monometallic catalyst. Furthermore, the peak corresponding to Pt^o for the W-Pt/C and the Co-Pt/C was more intense than that for Ni-Pt/C and Pt/C. The Co(2p$_{3/2}$) had the most intense peak at 782.9 eV (a shift of 4.5 eV from 778.4 eV of Co^o [36]) indicating the presence of oxidized metal species on the catalyst surface. For IAC, the oxygen content of bimetallic catalysts was greater than that of monometallic Pt/C catalyst. This can be attributed to the presence of oxidized species of the second metals, e.g., Ni, Co or W. Although the samples were prepared with an atomic ratio of 1:1 between Pt and the second metal, the XPS data showed that the second metal, i.e., Co and Ni, was more abundant than the first metal, i.e. Pt, on the surface of the deposited catalyst. Arico et al. [36] and Toda et al. [39] proposed a sandwich like structure with Pt forming protective skin over the second metal, which is positioned in underlying layers. The diffusion of the second metal into the bulk catalyst,

Table 2
Comparison of perchlorate reduction rates and the activation energy from various studies

	T (°C)	C_o (ClO$_4^-$) (mg L^{-1})	k'	E_a (h^{-1})	Ref. (kJ mol^{-1})
Co-Pt/C[a]	25	12.35[b]	1.5×10^{-1}	39.5	This study
	75	12.35[b]	1.6		
Re-Pd/AC	25	200	3.4×10^{-1}	–	[17]
Nano Fe^o	25	200	1.3×10^{-3}	79.2	[11]
	75	200	1.5×10^{-1}		
FeCl$_3$–HCl	110	10,000	$2.0–5.0 \times 10^{-3c}$	120.2	[10]
Ti(III)	40	50,000	8.9×10^{-2}	74.8–84.2	[44]

[a] In the gas phase.
[b] Surface bound concentration (mg g^{-1}).
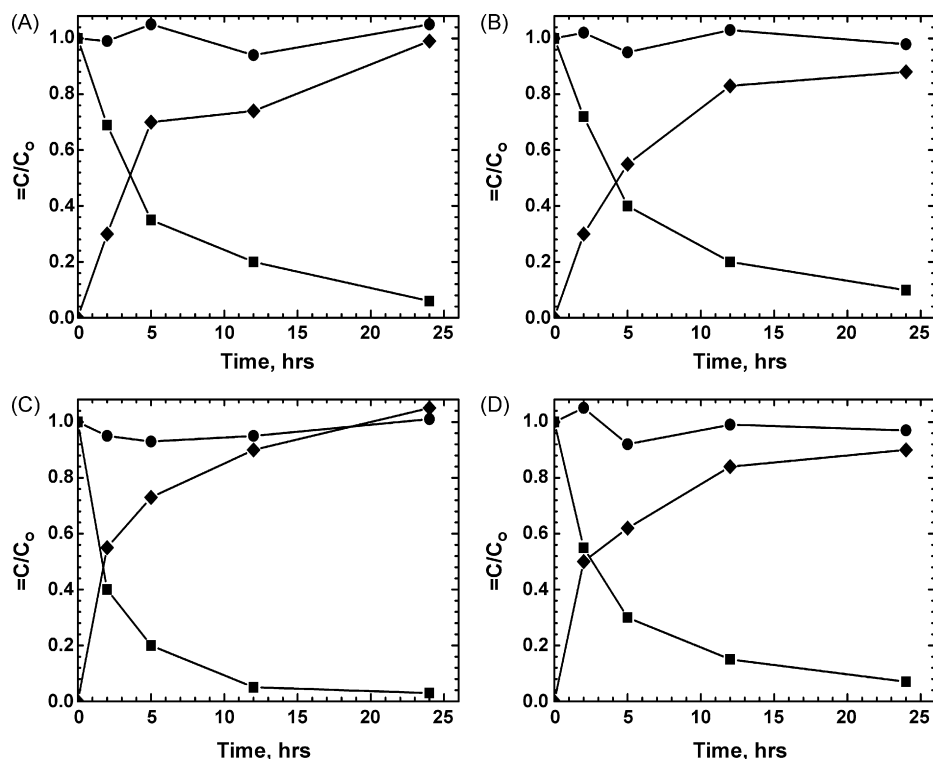[c] At various iron loadings.

Fig. 5. Chloride balance for the gas-phase perchlorate reduction on Pt based catalysts supported on activated carbon (50 °C). Symbols: (■): perchlorate reduction, (◆): chloride evolution, and (●): balance. (A) Pt/C, (B) Ni-Pt/C, (C) Co-Pt/C, and (D) W-Pt/C.

however, was also shown to be dependent on the annealing temperature [32,40]. Menning et al. [40] showed that substantial diffusion of Ni and Co into bulk Pt occurred at temperature above 500 K. Since in our experiments the catalysts were annealed only up to 563 K it is reasonable to speculate that fraction of the second metal was located on the Pt surface.

The XPS spectra were also collected for the catalysts after the adsorption/reduction experiments as well. The increase in the Pt saturation IAC surface after the perchlorate reduction was accompanied by the decrease in the concentration of the second metal (Table 3). After adsorption and reduction

Fig. 6. Effect of surface loading ($\equiv C/C_m$) of perchlorate on reduction efficiency (η) on Ni-Pt/C at different temperatures. Lines represent linear regression.

experiments the relative atomic percent of the second metal decreased by a factor of two for the bimetallic catalysts whereas the atomic percent of Pt increased. The loss of the second metal could be due to dissolution indicating that the second metal was not stable on the catalyst surface under the experimental conditions. On the contrary, Pt was tightly held onto the support surface. Toda et al. [39] showed that the second metal was easily lost from the surface layers of bimetallic alloys of Pt/Co and Pt/Ni under acidic conditions whereas the bulk portion was protected by the Pt films. In our study, the results of EDX analysis (not given), which is more sensitive to bulk composition of elements, also showed similar decrease in the second metal concentration. On the other hand, activated carbon is highly porous material, which internal pores constitute a greater portion of the total surface area. The majority of the metal catalysts is presumably deposited in the inner pores and cannot be detected by the XPS and EDX analysis. Therefore, the relative concentrations reported herein (Table 3) only represented a small fraction of the total metal catalysts impregnated in the activated carbon. The portion of catalyst that located on the outer surface of activated carbon may be more prone to loss due to dissolution or erosion. Despite the loss of some portion of the second metal the catalysts retained its initial activity for perchlorate reduction as evident by the relatively unchanged reduction efficiency when the catalyst was recycled and reused for multiple times. This might be due to the loss of the catalyst that was located on the outer surface of the support, while those deposited in the inner pores were intact.
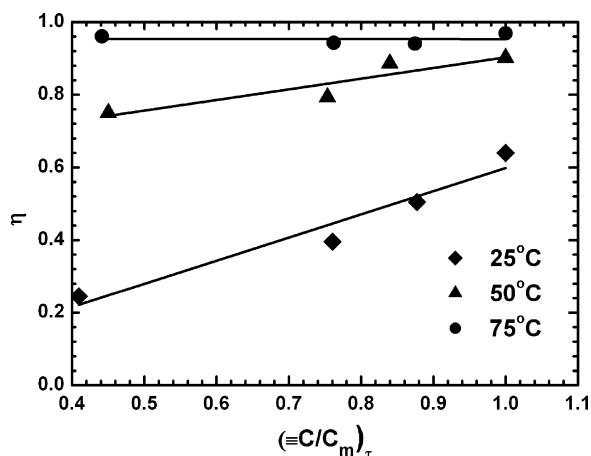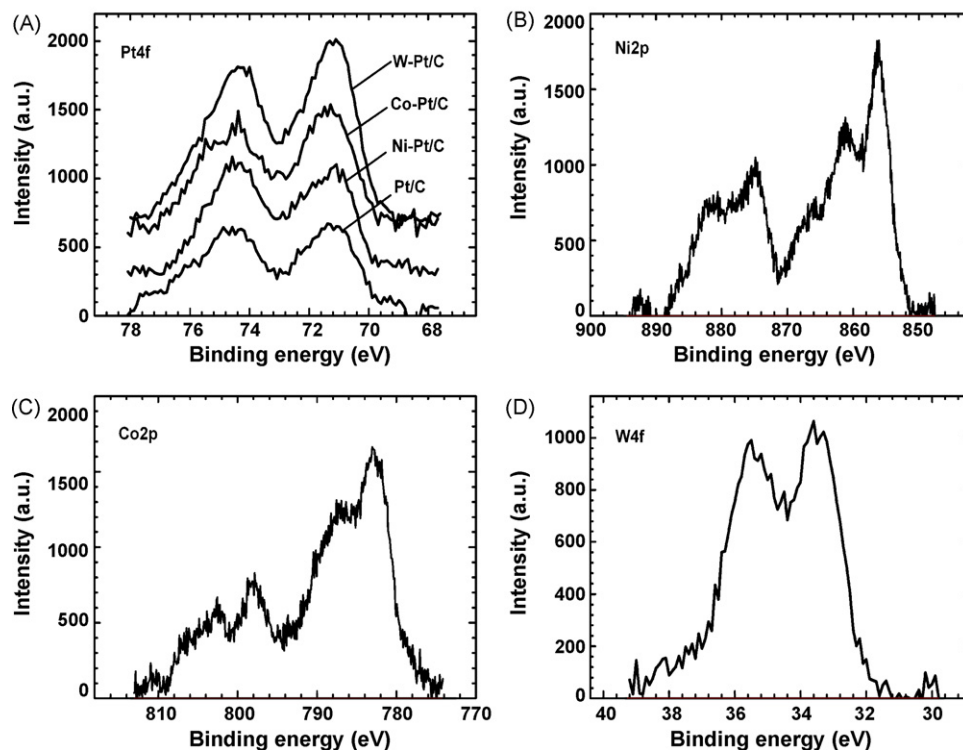
Fig. 7. XPS spectra of metal catalysts supported on activated carbon. (A) Pt 4f in mono- and bimetallic alloys supported on activated carbon; (B) Ni2p in Ni-Pt/C; (C) Co 2p in Co-Pt/C; and (D) W 4f in W-Pt/C.

3.5. Mechanistic aspects

To gain insight into the mechanistic aspect of the reduction of perchlorate, a series of control experiments were conducted with VAC and IAC under N_2 and H_2 atmosphere. Fig. 8 shows the results of the reduction of perchlorate in hydrogen and nitrogen atmosphere on the surface of VAC and Ni-Pt/C. It is well known that activated carbon, depending on the activation process can have a reduced (e.g., the H-type) or oxidized (e.g., the L-type) surface [34]. In our study, the activated carbon Filtrasorb F400 used as support was of the H-type that possessed a reduced surface and potentially was capable of participating in the reduction reaction directly. Asami et al. [41], Huang et al. [42] and Siddiqui et al. [43] have showed that such activated carbon is capable of reducing BrO_3^- in aqueous solution. Perchlorate is much more persistent than many other

anions and is very inert in dilute aqueous systems. In these experiments, the perchlorate loaded VAC, when removed from solution and exposed to various gas environments, was capable of reducing perchlorate even in the presence of inert gas such as nitrogen, but only at temperatures above 100 °C. Slight reduction of perchlorate was achieved when perchlorate laden VAC was exposed to hydrogen gas at 75 °C. Approximately 20% of perchlorate was reduced when Ni-Pt/C catalyst was used under N_2 atmosphere, which indicates that certain metals could reduce perchlorates directly. The exposure of perchlorate laden IAC to H_2 gas resulted in a sharp increase in perchlorate reduction. Based on the results of the present study it is clear that hydrogen gas activated on metal catalysts was the major reducing agent. Because a significant portion of the second metal was located on the surface of the catalysts, the role of metals as direct electron donors for perchlorate reduction cannot

Table 3
Surface composition of impregnated activated carbon (IAC) as prepared and after hydrogenation reduction as determined by XPS analysis

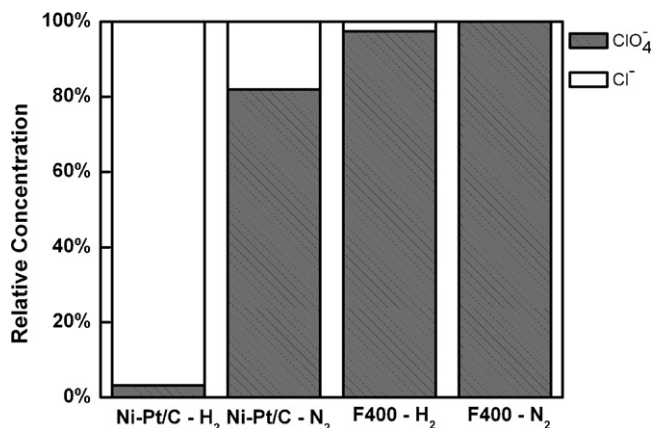| Element	Surface composition (%)								
	VAC	Pt/C		Ni-Pt/C		Co-Pt/C		W-Pt/C	
	A	A	B	A	B	A	B	A	B
Carbon	96.80	90.79	91.99	86.90	89.12	87.63	86.44	87.85	87.80
Oxygen	3.20	8.84	7.65	10.83	9.73	10.49	12.21	11.44	11.73
Pt	–	0.37	0.36	0.23	0.25	0.36	0.39	0.25	0.28
Second metal	–	–	–	2.04	0.90	1.53	0.96	0.46	0.19

A: as prepared; B: after experiment.

Fig. 8. Reduction of perchlorate by virgin and impregnated activated carbon under hydrogen and nitrogen atmosphere.

be ignored. The following equations can be written to describe the overall perchlorate reduction on the IAC surface:

$$\equiv ClO_4^- + 4H_2 \leftrightarrow Cl^- + 4H_2O \tag{4}$$

$$\equiv M^\circ + ClO_4^- \rightarrow \equiv MO_x + ClO_{4-x}^- \tag{5}$$
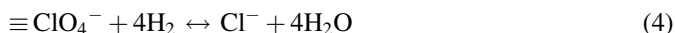
The amount of perchlorate reduced under nitrogen atmosphere on Ni-Pt/C was attributed to reduction by direct electron transfer from the surface metals to perchlorate as shown in Fig. 8 (approximately 20%). The difference between the total amount of perchlorate reduced on Ni-Pt/C under hydrogen and nitrogen could be attributed to hydrogen, which contributed approximately 75–80% of the total amount of perchlorate reduced. An extremely slow reduction of perchlorate in aqueous solutions under similar temperature conditions indicates that the formation of complexes between the bound perchlorate and the activated carbon and/or metals is important for perchlorate reduction. It is known that perchlorate does not form complexes easily [6]. However, exposing the perchlorate laden (wet) IAC to hydrogen atmosphere under elevated temperature could aid in the removal of water molecules from the surface, which will facilitate the formation of inner-sphere complexes between perchlorate and specific surface sites on the activated carbon. This will enhance the reduction of perchlorate directly by the metal or the catalyzed hydrogen. The notion implying the formation of innersphere complexes is consistent with what were reported by Harley and Sharpley [17], who suggested the formation of complexes, presumably of the inner sphere type, between perchlorate and Re(V) on the Pd-Re/AC catalyst surface. They reported a strong pH effect on the reduction of perchlorate by hydrogen gas in the presence of Pd-Re/AC catalyst. The perchlorate reduction rate constant decreased by a factor of 6–9 when the pH increased by 1 unit, e.g., from 2.67 to 3.67. This clearly indicates the importance of perchlorate adsorption on its reduction. It is know that the adsorption of anions such as perchlorate on activated carbon is favored at low pH. Therefore, it is expected that pH will play a significant role on perchlorate reduction. The context that perchlorate adsorption is a necessary step prior to reduction reaction is reflected by increase in reduction rates at acidic pH condition. This is in contrast to the perchlorate reduction in the

gas phase, where rates are independent of pH. As described in Eqs. (3)–(5) the overall perchlorate reduction efficiency is a function of the surface concentration of perchlorate, the uptake of hydrogen (catalyst dispersion) by IAC, and the temperature. Eqs. (4) and (5) do not explicitly show the effect of the proton; nonetheless, the pH-dependence of perchlorate adsorption and the surface charge of the activated carbon clearly indicate the importance of pH to the total process of perchlorate reduction.

4. Conclusions

Mono- (Pt/C) and bimetallic (Co-Pt/C, Ni-Pt/C, and W-Pt/C) Pt based hydrogenation catalysts were prepared and used to reduce perchlorate under hydrogen gas environment. The pH_{zpc} of activated carbon decreased from 9.2 to <3 after catalyst impregnation due to oxidation taking place during IAC preparation. The oxidation and plugging of micropores of activated carbon decreased the perchlorate adsorption on IAC by three-fold compared to VAC. Nonetheless, the reduction of perchlorate improved dramatically in the hydrogen gas phase compared to that in aqueous phase. The reduction of perchlorate was dependent on the perchlorate loading, temperature, and reaction time. The reduction kinetics was well fitted by the pseudo first order rate equation. The activation energies were two to three times lower than those reported by other researchers who studies perchlorate reduction in the aqueous phase; this indicated clearly the high efficiency of the present process. The reduction efficiency increased linearly with increase in perchlorate loading at low temperatures of 25 °C and was independent of perchlorate loading at temperatures above 75 °C.

The results of XPS analysis showed that relative oxygen content of IAC increased by a factor of two compared to VAC. This was due to the oxidation of activated carbon during the catalyst annealing under air and the presence of oxidized metal species. The XPS results also showed that Pt in mono- and bimetallic alloys was present in the metallic form while the second metals, e.g., Co, Ni, and W were mostly present in oxidized form. The XPS analysis of IAC before and after adsorption reduction experiments also showed that some portion of the second metals was lost from the catalyst surface due to dissolution and/or erosion. The Pt, however, was very stable and its relative surface abundance did not change or in some cases slightly increased due to the loss of other compounds.

Hydrogenation and direct reaction with the second catalytic metal took place with hydrogenation being responsible for ca. 80–85% of total perchlorate reduction whereas direct metal reduction accounted for the remaining ca. 15–20%. The gas-phase reduction of perchlorate on activated carbon impregnated with Pt based mono- and bimetallic catalysts was efficient in destroying perchlorate and superior to that when applied in the liquid phase.

Acknowledgements

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